Thermal Batteries Session

REVIEW OF CHLOROALUMINATE SYSTEMS FOR THERMAL BATTERY APPLICATIONS

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MAR 6 1984

AD A138565

Introduction

Production thermal batteries conventionally use LiCl—KCl electrolyte and therefore operate only at very high temperatures ($400°$-$600°$ C). Use of this highly conductive, high temperature electrolyte maximizes available current densities but imposes a severe thermal stress on surrounding components. Excellent insulation is required to insure an active life of more than a few minutes.

We have found the equimolar NaCl—AlCl₃ mixture to be a reasonable electrolyte at much lower operating temperatures where low to moderate current densities can be tolerated. Single cell studies made over a temperature range of $175°$-$275°$ C and a current density range of 15-150 mA/cm² showed that LiAl was a suitable anode material, and chlorides of copper(II), iron(III), and molybdenum(V) were suitable cathode materials. The Eureka Company, under Air Force contract, has successfully built and tested thermal batteries based on chloroaluminate electrolytes.

This paper reviews relevant characteristics of chloroaluminate electrolytes, summarizes single cell research, describes present status of battery development, and indicates areas of current research.

Properties of Chloroaluminate Electrolytes

Aluminum chloride reacts exothermally with alkali metal chlorides to form the ionic chloroaluminates, $AlCl_4^-$ and $Al_2Cl_7^-$. The relative amounts of $AlCl_4^-$ and $Al_2Cl_7^-$ present depend upon the initial ratio of AlCl₃ to MCl and, in fact, appreciable unreacted AlCl₃ remains (as $Al_2Cl_6^*$) at very high initial AlCl₃:MCl ratios (1).

At all reasonable melt temperatures, the concentrations of $Al_2Cl_7^-$ and Al_2Cl_6 are negligibly small when AlCl₃ and MCl are reacted in equal molar amounts. For example, at $175°$ C, $X_{Al_2Cl_7^-} = X_{Cl^-} = 1.4 \times 10^{-4}$ and $X_{Al_2Cl_6} = 3.6 \times 10^{-9}$ when MCl is NaCl (1). When MCl is LiCl, $X_{Al_2Cl_7^-} = X_{Cl^-} = 7 \times 10^{-3}$ (2); $X_{Al_2Cl_6}$ is also very small in the AlCl₃—LiCl system (3). Vapor pressures of the equimolar mixtures are very low (4,5), and may be neglected in the thermal battery environment.

The electric conductivities of NaCl—AlCl₃ and LiCl—AlCl₃ mixtures are the greatest at or very near the equimolar composition. At $175°$ C, for example, $\kappa = 0.378$ (6) and 0.325 ohm⁻¹ cm⁻¹ (7), respectively for the two systems. Viscosities of the equimolar mixtures also are low [$\eta = 2.827$ (8) and 3.834 mPas (9), respectively, at $175°$ C] and rise as the AlCl₃:MCl ratio becomes greater than one. The two equimolar mixtures melt at $152°$ and $142°$ C, respectively.

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*At pressures and temperatures encountered with thermal batteries, unreacted AlCl₃ is virtually completely dimerized and exists in liquid and gas phases and in solutions as Al_2Cl_6.

In practice, the electrolytes are not exactly $NaAlCl_4$ and $LiAlCl_4$, for it is convenient to saturate the melts with NaCl and LiCl, respectively. The solubility limits are very near the equimolar compositions, and all of the properties cited above differ negligibly in saturated solutions and equimolar solutions. The solubilities are slightly temperature dependent; at $175°$ C $X_{AlCl_3} = 0.4975$ for NaCl(satd)—AlCl₃ (10), and 0.4925 for LiCl(satd)—AlCl₃ (11). Unless specifically stated otherwise, all following references to electrolytes will assume alkali-saturated mixtures.

Limited study has been made in our laboratory of mixed NaAlCl₄—LiAlCl₄ electrolytes. All of the desirable properties cited appear to be retained in such mixtures, except melting point. In fact, the melting point drops rather sharply to slightly over $100°$ C for the eutectic composition (5) which would be even more advantageous for long life applications.

Single Cell Studies

The experimental work on anode and cathode materials was performed using single cells of the same type that would be expected to be used (in stacks) in an actual battery. This approach allowed us to quantitatively recognize the interdependence of anode-electrolyte-cathode in cell optimization.

EXPERIMENTAL

Detailed discussions on electrolyte preparation, cell fabrications, and discharge experiments have been presented earlier (12-14).

Single cells were fabricated as three-layer pellets consisting of an anode layer, a cathode layer, and a separating electrolyte layer. The separating electrolyte layer consisted entirely of electrolyte-binder mixture (EBM) which was composed of 90 weight percent (w/o) electrolyte and 10 w/o SiO₂ binder. The cathode layer was a mixture of EBM, graphite, and active cathode material. The anode layer usually contained in addition to the active anode material, a small amount of EBM to facilitate pelletizing. Single cell configuration is shown schematically in Figure 1.

Single cells were discharged at constant current between heated platens. Cell performance was measured by calculating the energy density at 80% of initial closed circuit voltage and based on cell weight.

ANODE STUDIES

Materials initially investigated for use as anodes included aluminum, lithium, and LiAl alloys of various compositions. As shown in Figure 2, the discharge behaviors of lithium and LiAl were superior to that of aluminum; however, the lithium-containing anodes experienced a high voltage "spike" during cell activation, as seen in Figure 3. Two features of these

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ANODE: | Li Alloy Foil
or
Li Alloy Powder and EBM[*]

SEPARATOR: | EBM[*]

CATHODE: | $CuCl_2$ or $FeCl_3$ or $MoCl_5$
Graphite Flakes
EBM[*]

[*]**EBM:** | 90 wt% Electrolyte
10 wt% Silica

Figure 1. Single cell configuration

Figure 3. Activation voltage behavior for aluminum and lithium-containing anodes.

activation plots bear special notice. First is that the spike appears below the electrolyte melting point, then sharply decays to the aluminum potential at the melting point. The second important characteristic is the much smaller cell polarization during discharge noted for cells containing lithium-aluminum alloy. The superior performance of LiAl seen in Figure 2 is a reflection, at least in part, of the low cell polarization characteristics of LiAl. The high voltage spike has been attributed to a displacement reaction between lithium in the anode and the molten electrolyte (15)

$$3\ Li + NaAlCl_4 \rightarrow 3\ LiCl + NaCl + Al$$
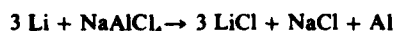
Several lithium-aluminum alloy compositions were investigated (14,15). The best performance was given by the alloy 60.2 atomic percent (a/o) (28 w/o) lithium. This alloy was used in subsequent optimization studies of other cell components.

The actual role of the lithium in the anode is not clear, but there is indirect evidence that it is the lithium itself that is actually reacting during cell discharge, perhaps by the reaction above. Total energy output of single cells was proportional to the amount of lithium initially present in the anode. Furthermore, the melting point of the electrolyte in discharged cells
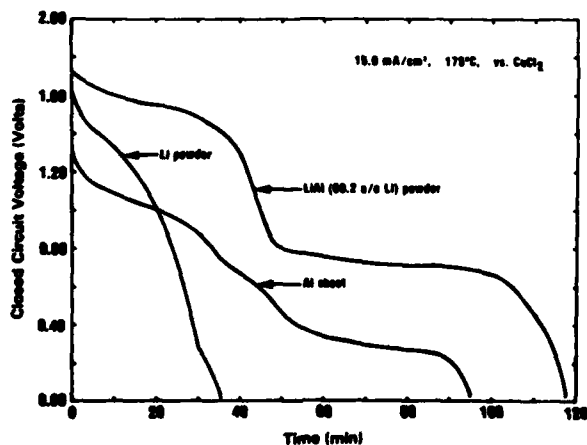
was substantially lowered, as much as 30° C in some cases, implying the addition of some foreign component, e.g., Li^+. Carpio and King (16) have shown that lithium can be electrochemically removed from LiAl into a LiCl(satd)—$AlCl_3$ electrolyte.

Recently, LiSi and LiB have been tested and their performance compared with LiAl. The energy densities obtained from $LiSi/CuCl_2$ cells were essentially the same as for $LiAl/CuCl_2$ cells at all operating conditions. These data are shown in Figure 4 for high and low current densities. Internal resistances determined from cell polarization data are given in Table I.

Experiments with LiB anodes were limited to a single temperature (200° C) and to current densities of 15–100 mA/cm² because of limited availability of LiB. Figure 5 shows that energy densities for $LiB/CuCl_2$ cells were slightly higher than for $LiAl/CuCl_2$ cells at most current densities. This was due in part to the weight difference between the two cell types. The LiB was supplied as finished anodes of about 0.16g LiB pressed on to a stainless steel substrate, whereas the lightest LiAl anode we could fabricate contained 0.27g LiAl. However, at 100 mA/cm², the $LiB/CuCl_2$ cell energy density is significantly higher than the $LiAl/CuCl_2$ cell. Insufficient data were available to calculate $LiB/CuCl_2$ cell resistances.

While our study indicates that LiB may be the superior anode for chloroaluminate thermal batteries, additional work is needed to fully explore this possibility.
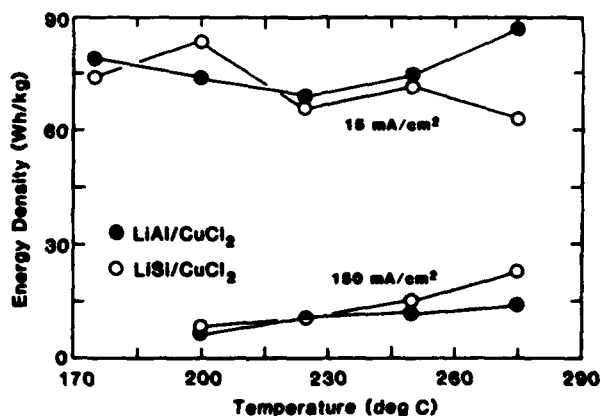
Figure 2. Discharge curves for aluminum, lithium, and lithium-aluminum anodes.

Figure 4. Comparison of $LiSi/CuCl_2$ and $LiAl/CuCl_2$ cells at 15 and 150 mA/cm².

TABLE I
SINGLE CELL INTERNAL RESISTANCES

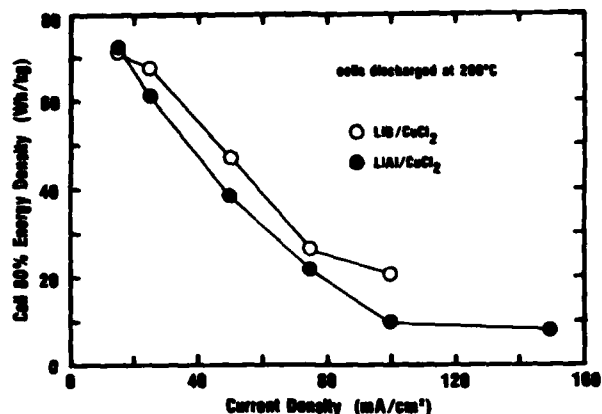| Temperature (°C) | Internal Resistance (Ω) | |
	$LiAl/CuCl_2$	$LiSi/CuCl_2$
175	0.89	0.96
200	0.32	0.35
225	0.32	0.34
250	0.31	0.28
275	0.29	0.28

Figure 5. Comparison of $LiB/CuCl_2$ and $LiAl/CuCl_2$ cells

CATHODE STUDIES

In studies of over 40 inorganic sulfides, oxides, and halides, $MoCl_5$, $CuCl_2$, and $FeCl_3$ were identified as good cathode materials for chloroaluminate thermal cells (13,17). Consequently, these three materials were studied extensively in optimized single cells (14,15,18).

The open-circuit potentials were 2.4, 2.3, and 1.8V, respectively, for $LiAl/MoCl_5$, $LiAl/FeCl_3$, and $LiAl/CuCl_2$ cells. Internal resistances of the three cells types were similar; at 200° C, for example, single cell resistances were 0.63, 0.5, and 0.42 Ω, respectively.

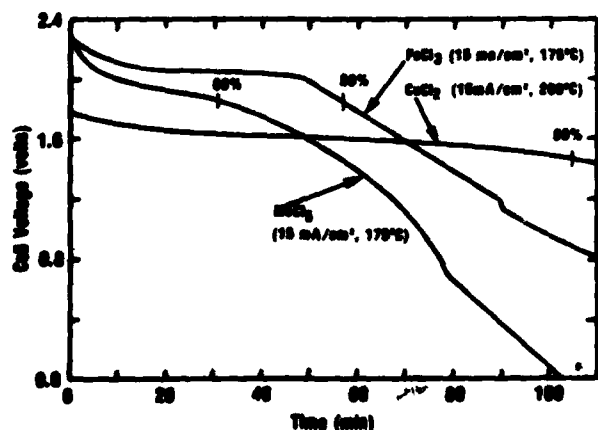Even though $CuCl_2$ produced the lowest potential, it pro-
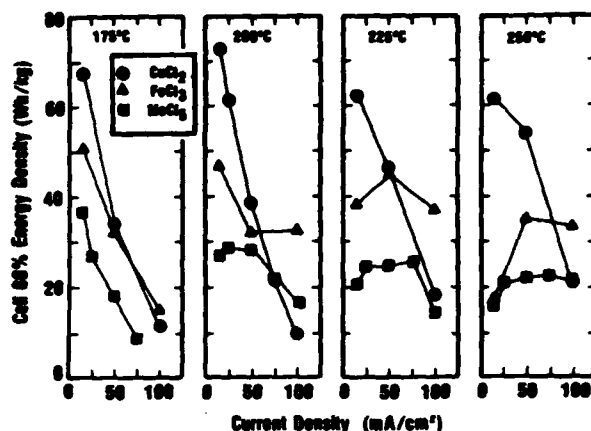

Figure 7. Energy densities of $LiAl/CuCl_2$, $LiAl/FeCl_3$, and $LiAl/MoCl_5$ cells.

duced the highest energy density, over 80 W-hr/kg, due to a much longer lifetime (110m at 15 mA/cm²). The discharge curves and operating conditions for the best cell of each type are compared in Figure 6. Figure 7 shows the energy densities for the three cell types over the complete range of operating conditions. At low current density, $CuCl_2$ clearly showed greater energy densities than the other two cathodes. At high current density, $FeCl_3$ was the superior cathode while $CuCl_2$ and $MoCl_5$ were similar in performance.

Another performance criterion examined was the temperature tolerance of the different cells. The ideally temperature tolerant cell would be one in which the energy density did not change over the operating temperature range. As a measure of the performance change over the temperature range, we defined the percent change in performance, at a given current density, as

$$\frac{\text{maximum energy density} - \text{minimum energy density}}{\text{maximum energy density}} \times 100$$

A comparison of the three cell types in this way is shown in Figure 8. At low current density, $CuCl_2$ was the cathode most tolerant to temperature changes (smallest percent change
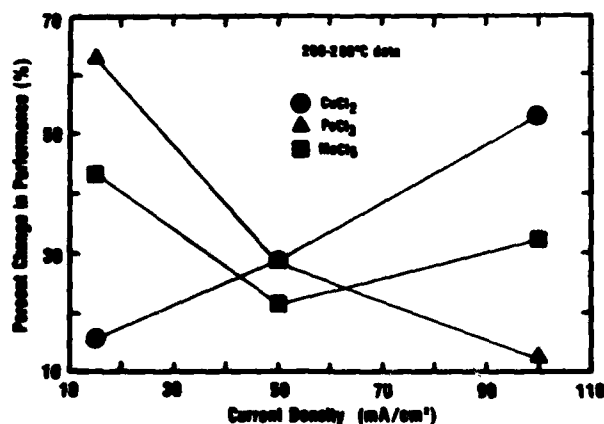

Figure 6. Comparison of discharge curves for the best cell of each of the three cell types.

Figure 8. Temperature tolerance (measured as percent change in performance) of the three cell types.

in energy density), and Fe^{3+}, was the least tolerant. At high current density, the reverse was true.

The conclusion can be made from these findings that LiAl/CuCl$_2$ cells are more suited to low current density applications, while LiAl/FeCl$_3$ cells are more suited to high current density applications.

Development of a Chloroaluminate Thermal Battery

In 1976, the Air Force Aero-Propulsion Laboratory awarded a contract to the Eureka Company to investigate the feasibility of a thermal battery based on the system LiAl/NaAlCl$_4$/MoCl$_5$. This initial contract work resulted in a battery that had all the operating characteristics of then existing thermal batteries, plus the advantage of lower operating temperature and longer life (19).

Effort continued toward a fully engineered battery, but by 1978, tests had shown MoCl$_5$ to be unsuitable for use in thermal batteries because of severe performance degradation after battery storage at elevated temperature. The cause of this degradation is still not fully understood, but it appeared to result from decomposition or vaporization of the MoCl$_5$. Also, FeCl$_3$ was rejected at this time because of difficulties encountered in the assembly of single cells using this compound. Thus MoCl$_5$ and FeCl$_3$, which were considered good cathode materials electrochemically, were found unsuitable for use in thermal batteries; whereas CuCl$_2$, considered less desirable electrochemically, remained as the best practical cathode material.

Engineering work continued with CuCl$_2$ as the cathode material, different electrolyte compositions, and LiAlCl$_4$ as an alternate electrolyte. Much of this work was concerned with eliminating the activation voltage spike. This effort was successful through anode additives and changes in cell composition. By the end of 1979, an optimum cell design had been identified. The anode was a mixture of 65 w/o LiAl and 35 w/o magnesium powder. The cathode was a mixture of 70 w/o CuCl$_2$, 15 w/o graphite, and 15 w/o AlCl$_3$-rich electrolyte.* The separating electrolyte was LiAlCl$_4$. This optimized cell produced 1.80V at 13 mA/cm^2 and an average energy density of 55-60 W-hr/kg (20). Batteries using these cells meet essentially all program goals.

Tests have shown that during activation and discharge of these batteries, the maximum temperature at the edge of the cell stack was 250° C (20). This low operating temperature remains as the principal advantage of the chloroaluminate thermal battery. However, one must recognize that reaction kinetics are temperature dependent and that to achieve lower temperatures, some performance must be sacrificed. Accordingly, a direct performance comparison between chloroaluminate systems and LiCl—KCl systems is not possible. Consi-

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*The electrolyte was nominally 52:48 AlCl$_3$:NaCl. This translates to 92 mole percent (m/o) NaAlCl$_4$ and 8 m/o NaAl$_2$Cl$_7$.

derations must be given to the particular application requirements of current density, volume, weight, and lifetime.

Areas for Future Study

There are two principal areas in which future work will be directed. First, additional studies using LiB anodes will begin when this material becomes available. Single cell tests over the full temperature and current density ranges are needed to fully evaluate LiB as an anode material and to compare it to the other anode materials.

The second area is the study of molybdenum complex ions such as MoCl$_6^-$ and MoCl$_6^{2-}$ as stable molybdenum cathodes.

REFERENCES

1. A. A. Fannin, Jr., L. A. King, and D. W. Seegmiller, *J. Electrochem. Soc.*, **119**, 801 (1972).
2. G. Torsi and G. Mamantov, *Inorg. Chem.*, **11**, 1439 (1971).
3. R. A. Carpio, H. A. Øye, A. A. Fannin, Jr., and L. A. King, To be published.
4. J. T. Viola, L. A. King, A. A. Fannin, Jr., and D. W. Seegmiller, *J. Chem. Eng. Data*, **23**, 122 (1978).
5. R. A. Carpio, R. K. Bunting, and L. A. King, Unpublished work.
6. R. A. Carpio, F. C. Kibler, Jr., L. A. King, K. Tørklep, and H. A. Øye, Submitted for publication.
7. R. A. Carpio, L. A. King, F. C. Kibler, Jr., and A. A. Fannin, Jr., *J. Electrochem. Soc.*, **126**, 1650 (1979).
8. W. Brockner, K. Tørklep, and H. A. Øye, *Ber. Bunsenges. Phys. Chem.*, **83**, 1 (1979).
9. K. Tørklep and H. A. Øye, To be published.
10. G. Torsi and G. Mamantov, *Inorg. Chem.*, **19**, 1900 (1971).
11. R. A. Carpio, L. A. King, and A. A. Fannin, Jr., *J. Chem. Eng. Data*, **24**, 22 (1979).
12. G. D. Brabson, J. K. Erbacher, L. A. King, and D. W. Seegmiller, FJSRL Technical Report 76-0002, F. J. Seiler Research Laboratory (AFSC), USAF Academy, CO, 1976; AD 021664.
13. C. L. Hussey, J. K. Erbacher, and L. A. King, FJSRL Technical Report 76-0003, F. J. Seiler Research Laboratory (AFSC) USAF Academy, CO, 1976; ADA 021748.
14. J. C. Nardi, J. K. Erbacher, C. L. Hussey, and L. A. King, *J. Power Sources*, **3**, 81 (1978).
15. J. K. Erbacher, C. L. Hussey, and L. A. King, in Proc. 28th Power Sources Symposium, Atlantic City, p. 84 (1978).
16. R. A. Carpio and L. A. King, To be published.
17. J. C. Nardi, J. K. Erbacher, and C. L. Hussey, FJSRL Technical Report 77-0004, F. J. Seiler Research Laboratory (AFSC), USAF Academy, CO, 1977; ADA 043659.
18. R. L. Vaughn, J. C. Nardi, J. K. Erbacher, C. L. Hussey, and L. A. King, in "Battery Design and Optimization," S. Gross, Editor, p. 401, The Electrochemical Society Softbound Proceedings Series, Princeton, N.J. (1979).
19. D. M. Ryan and L. C. Bricker, AFAPL Technical Report-77-12, Air Force Aero-Propulsion Laboratory, Wright-Patterson AFB, OH, 1977.
20. D. M. Ryan, Progress Report: Advanced Thermal Batteries. Contract No. F33615-77-3147, The Eureka Co., Bloomington, IL, January, 1980.